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Separation of Fischer-Tropsch Wax Products from Ultrafine Iron Catalyst Particles

Technical Progress Report

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ABSTRACT

In this reporting period, a fundamental filtration study was continued to investigate the separation of Fischer-Tropsch Synthesis (FTS) liquids from iron-based catalyst particles. The overall focus of the program is with slurry-phase FTS in slurry bubble column reactor systems. Hydrocarbon products must be separated from catalyst particles before being removed from the reactor system. An efficient wax product/catalyst separation system is a key factor for optimizing operating costs for iron-based slurry-phase FTS. Previous work has focused on catalyst particle attrition and the formation of ultra-fine iron carbide and/or carbon particles. With the current study, we are investigating how the filtration properties are affected by these chemical and physical changes of the catalyst slurry during activation/synthesis.

The shakedown phase of the pilot-scale filtration platform was completed at the end of the last reporting period. A study of various molecular weight waxes was initiated to determine the effect of wax physical properties on the permeation rate without catalyst present. As expected, the permeation flux was inversely proportional to the nominal average molecular weight of the polyethylene wax. Even without catalyst particles present in the filtrate, the filtration membranes experience fouling during an induction period on the order of days on-line.

Another long-term filtration test was initiated using a batch of iron catalyst that was previously activated with CO to form iron carbide in a separate continuous stirred tank reactor (CSTR) system. The permeation flux stabilized more rapidly than that experienced with unactivated catalyst tests.

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EXECUTIVE SUMMARY

In this reporting period, a fundamental filtration study to investigate the separation of Fischer-Tropsch Synthesis (FTS) liquids from iron-based catalyst particles was continued. Catalyst consumption due to filtration losses is a major expense in the operation of slurry phase FTS reactors using iron-based catalysts. Attrition of such catalysts in slurry-phase reactors produces a significant amount of fines, making catalyst separation from the products difficult. During slurry-phase FTS with bubble column reactors, catalysts are generally separated from accumulated reactor wax by either internal filtration or an external settling system which circulates catalyst back to the reactor. Catalyst fines produced by attrition may cause filters to plug and are difficult to separate by settling. As a result, multiple filtration stages are needed in order for the waxes to be well-suited for down-stream processing.

The overall objective of this filtration study is to test the effectiveness of various cross-flow filtration procedures with a simulant FTS slurry. The wax products from a FTS reactor can vary widely depending on the type of process implemented. In this study, the focus is on high-alpha iron-based slurry-phase reaction processes. The change in filtration properties of iron catalyst slurries will be correlated with physical and chemical changes of the particles during Fischer-Tropsch conditions.

For first two years of this program, a state-of-the-art filtration test platform is being utilized to study effect of process parameters, slurry chemical/physical changes, and filter media on the permeate flux and quality (based on Fe content). Additionally, flux maintenance procedures are being developed to maintain the highest achievable permeation rate over the lifetime of the filter membranes. The unit is capable of testing slurry batches as large as 98 liters (26 gallons). This unit will allow several types of cross-flow filter media to be researched under simulated FTS conditions at flowrates from 4 to 20 lpm. The cross-flow filtration modules are zirconia-coated steel membranes having a nominal pore size of 0.1 μm. In year 3 of the program, a prototype filtration system will be retrofitted to an existing SBCR to test the efficacy of the filtration procedures developed using the filtration test platform.

During the last reporting period, the shakedown phase of the program was completed. Early tests were focused on finding a suitable wax and catalyst slurry simulant for the pilot filtration unit. Initially, test slurries were processed using an unactivated, high alpha iron catalyst added to various mixtures of polyalphaolefins (Durasyn 164) and polyethylene waxes (a commercial line of products called Polywax, manufactured by Baker Petrolite). In these tests with unactivated catalyst, the lack of long-term flux stability was partly attributed to the fouling from the higher molecular weight components from the Polywax 3000 (with a nominal molecular weight of 3000 g/mole). Subsequent filtration test results with catalyst slurries prepared with Polywax 500 (average molecular weight 500 g/mole) displayed a similar flux decline over the first 100 hours time-on-stream.

In the current reporting period, a series of tests without catalyst were conducted using Polywax 500, 655, 725 and 855 (with average molecular weights of 500, 655, 725, and 855, respectively). The goal of this test was to quantify the effect of the wax molecular weight on the "clean" permeate flux. Additionally, the apparent fouling or induction period of each wax could be observed without the potential interference created by catalyst attrition. The test conditions for the "clean" wax tests were 4.2 m/s axial cross-flow velocity at 200 ^{o}C; the TMP was varied from 0.7 to 1.7 bar. The permeate flux of the Polywax 500 became stable after dropping from 0.9 to 0.65 lpm/m^2 after 5 days at 1.4 bar TMP. Subsequent test results with the higher molecular weight waxes indicated shorter, if any induction periods. However, the filter element was not removed and regenerated after the initial Polywax 500 test. Additional tests are planned to quantify the "clean-tube" induction period of Polywax 655.

The method used to determine slurry particle size distribution has been shown to have severe limitations. Slurry samples taken from the filtration unit had to extracted in o-xylene to remove the wax residue before being submitted for particle size analyses. Problems were encountered in recovering catalyst samples in the extraction thimbles (rated for 0.8 μm); over 30-50% of the catalyst particles passed through the extraction thimble indicating substantial attrition of the particles. Also, we reported that qualitative particle settling tests indicated that catalyst attrition is changing the slurry properties over the time-scale of the filtration tests. Accordingly, a filtration test run using iron catalyst that had been activated in a CSTR system was initiated. It was anticipated that the phase change to carbide form during activation in CO in addition to the increased physical attrition due to the CSTR agitator would result in a dramatic decrease in catalyst particle size. The flux stabilized to less than 0.2 lpm/m^2 over a 24 hour period as compared to 6 days with the unactivated catalyst.

In a separate ongoing investigation, insight into the mechanism (i.e., chemical and physical changes) of catalyst attrition is being studied for commercial development and eventual scale-up of the process. One proposed hypothesis is that Fe is lost from the surface of the catalyst as iron carbides (possibly the working active surface phase), which can blind the filters and result in detrimental pressure drop increases. Rigorous characterization is required to confirm any appropriate mechanism. In this reporting period, we are utilizing the EXAFS synchrotron method to characterize the chemical state of the Fe species present in the working catalyst. Furthermore, we continue to use EXAFS as an indirect approach to attempt an elucidation of the active Fe surface phase. Rubidium and potassium are alkali metals which promote the Fischer-Tropsch reaction catalyst by iron. However, rubidium, and not potassium, is an atom which can be studied at the Brookhaven beamline by EXAFS. Therefore, we have attempted to further understand the active phase of Fe by examining the local structure surrounding Rb. The work was conducted in part to refine our analytical methods which will be used in the near future to characterize used catalyst slurries.

TASK 1. Fundamental Filtration Studies

Task 1.1 Shakedown *(subtask completed)*

Task 1.2. Solvent wax experiments

INTRODUCTION

Traditionally, iron catalysts have been used for F-T synthesis when the syngas is coal-derived, because they have the ability to simultaneously carry out the WGS reaction. Thus, less hydrogen is required and oxygen exits the reactor in the form of CO_2. Cobalt suffers from a low WGS activity, making it unsuitable for general use with low H_2/CO ratio syngas feeds. Iron catalysts such as those used by Sasol are typically prepared by precipitation while cobalt catalysts are generally supported on high surface area oxides such as alumina, silica and titania. Both types of catalysts, and probably cobalt more so than iron, are very sensitive to sulfur poisoning. However, filtration issues in cobalt-based FTS reactors are less problematic since catalyst supports are more attrition resistant than that of iron-based systems.

Because the Fischer-Tropsch synthesis (FTS) reaction is so exothermic, one of the major problems in control of the reaction is heat removal. Recent work has concentrated on the use of slurry phase reactors which are able to solve the problem of heat removal from this very exothermic reaction, as well as use low H_2/CO ratio syngas, provide high catalyst and reactor productivity, permit catalyst regeneration, and have relatively simple designs and low initial costs.

Catalyst attrition is a major problem in the operation of slurry phase FT reactors using iron-based catalysts (1,2). Attrition of such catalysts in slurry reactors produces significant amount of fines, making catalyst separation from the products difficult, as the catalyst particles do not settle well. During slurry phase FTS with bubble column reactors, catalysts are generally separated from accumulated reactor wax by either internal filtration or an external settling system which circulates catalyst back to the reactor. Catalyst fines produced by attrition may cause filters to plug and are difficult to separate by settling. Ultimately, the long residence time of a catalyst particle in an industrial reactor is sufficient to break down catalyst particles. Therefore, a robust filtration system is needed for FTS to be a viable technology.

Generation of fines from a SBCR can occur in 3 stages: 1. The release of nascent fine particles from the surfaces of the bulk catalyst particle that were formed during catalyst preparation; 2. Initial products of attrition from physical breakage of the catalyst particles; and 3. On a longer time-scale, the formation of iron carbide crystallites. Each of these stages present unique filtration problems during the production of FTS wax.

Some limited fundamental studies have shown that attrition resistance of iron-based catalysts depends on the type of activation the catalyst receives. However, these studies have not attempted to correlate the change in filtration properties of catalyst slurries with physical and chemical changes of the particles under conventional FTS conditions. Iron-based Fischer-Tropsch catalysts undergo a series of phase transformations during activation and use.

Catalyst activation with carbon monoxide or syngas typically results in the conversion of Fe_2O_3 to Fe_3O_4 and ultimately to one or more carbides during reaction synthesis (1). Fine particles extracted from a FTS slurry are shown in Figures 1 and 2. The slurry samples were dissolved in ortho-xylene and subsequently evaporated over a lacy carbon substrate. As shown in Figure 1, the iron crystallite agglomerates can be as large as 0.2 to 1.0 μm. However, iron particles on the order of 10-20 nm are also predominant as shown in Figure 2. The mobility of these smaller nm-scale particles is unknown. During the filtration process, clusters of these particles may agglomerate and make for more efficient separation. It is also likely that a portion of these smaller crystallites migrate into the filter media and cause irreversible fouling.

Numerous separation processes have been proposed in the literature based on a variety of filtration media along with washing/cleaning techniques (3-7). Most of these filtration methods are for primary filtration (removing wax products with reduced catalyst concentration, below 2000 ppm). Secondary filtration should reduce the catalyst concentration below about 10-15 ppm such that the wax can be compatible with downstream processes such as cracking.

EXPERIMENTAL

Filtration Test Platform. An existing pilot plant platform was modified into a cross-flow filtration test unit. This unit, depicted schematically in Figure 3, will allow several types of cross-flow filter media to be researched under simulated FTS conditions. Three prototype filtration modules were received from Pall, Inc. The modules have an inlet (filtrate) and outlet (retentate) ports with ½" tubing ends, and a permeate port, located near the midpoint of the unit, as shown in Figure 4. The filters' stainless steel membranes have a nominal pore size of 0.1 μm. The surface of the filter media substrate is coated with a proprietary sub-micron layer of zirconia.

The filtration piping and instrumentation is heated via several circuits of copper heat-trace tubing. A Therminol 66 heat transfer fluid is circulated through the heat-trace tubing using an electrically-heated hot oil system. The temperature controller was calibrated to operate over a temperature range of 180 to 250 ^{o}C.

Data gathering and process control functions are accomplished by a National Instruments real-time computer system. A 98 liter (26 gallon) slurry mixing tank is heated by hot-oil circulation jacket. Slurry mixtures of catalyst and wax are loaded batch-wise into the system. A Moyno (progressive cavity) pump is used to circulate the mixture through the cross-flow filter element. A manually-actuated valve, located downstream of the filter element, maintains a slurry flow rate set-point of 2 to 40 lpm.

Unfiltered slurry (or retentate) passing through the filter tube is recycled to the mixing tank. The differential pressure across the filter medium or trans-membrane pressure (TMP) is automatically controlled by a let-down valve. The permeate can be recycled to the slurry tank for continuous filtration simulation (in order to maintain a constant solids concentration in the system) or can be collected and removed from the system to test semi-batch filtration schemes. The permeation rate is periodically measured by diverting the stream into a collection flask over a convenient time interval. Samples can be collected before the filter for characterization. In tests where the catalyst is activated, a gas pad of CO or syngas can be applied to the system otherwise the system vapor space is purged with inert gas such as argon or nitrogen. Slurry temperature, simulating the FTS activation conditions, can be controlled up to 240 °C. Modular filtration media can be tested under various filtration rates, differential pressures and operating modes. The system is designed so that the filter unit can be bypassed in order to change filters while the slurry continues recirculation.

A variety of precipitated catalyst slurries mixed with various molecular weight waxes (C_{30} to C_{100}) will allow a range of effective slurry viscosities to be studied (8). Olefins and alcohols will be doped into the catalyst slurry to test their influence on filtration properties. In addition, we are proposing that a series of filtration experiments with ultra-fine iron particles (less than 3 μm) for evaluating the "worst-case" scenario of wax/catalyst separation. Small sections of the filter media tested will be microscopically examined to determine the extent of ultra-fine particle penetration.

Filter Back-flush System. As shown in Figure 4, the back flush system consists of a piston pump that is triggered by a computer controlled timer. The back-flush fluid consists of cleaned permeate stored in a 40 ml tube bomb located near the suction side of the piston pump. This system will be used throughout the study to develop an optimum cleaning program that can sustain a permeate flux rate over a many days.

Static Permeation Apparatus. In order to quantify the degree of filter media fouling, we constructed a static permeation rig to test the permeability of the membranes before and after catalyst filtration tests. A schematic of the apparatus is shown in Figure 5. A 4-liter vessel filled with clean/filtered C_{30} oil is heated to a temperature between 180 to 220 ^oC. The C_{30} oil is commercial polyalphaolefin known as Durasyn 164, produced by Amoco. A differential pressure or an effective TMP can be varied across the filter membrane via helium gas through a pressure regulator. The resulting permeation rate of the C_{30} oil is measured. The curve of the membrane flux vs. TMP will provide a snapshot of the tube's fouling condition.

RESULTS AND DICUSSION

Clean Wax Permeation Study. As previously reported, test slurries were processed using an unactivated, high alpha iron catalyst added to various mixtures of polyalphaolefins (Durasyn 164) and polyethylene waxes. In these tests with unactivated catalyst, the lack of long-term flux stability was partly attributed to the fouling from the higher molecular weight components from the Polywax 3000 (with a nominal molecular weight of 3000 g/mole). Subsequent filtration test results with catalyst slurries prepared with Polywax 500 (average molecular weight 500 g/mole) displayed a similar flux decline over the first 100 hours time-on-stream. The lack of flux stability was attributed to two factors: 1. the fouling from the higher molecular weight component contributed from the Polywax 500 or 3000; and 2. from the mechanically induced attrition of the catalyst particles resulting in higher concentration of fines (below 1 μm).

A series of tests without catalyst were conducted using Polywax 500, 655, 725 and 855 (with average molecular weights of 500, 655, 725, and 855, respectively). The goal of this test was to quantify the effect of the wax molecular weight on the “clean” permeate flux. Additionally, the apparent fouling or induction period of each wax could be observed without the potential interference created by catalyst attrition. In Figure 6, carbon distribution plots for a high-alpha FTS iron catalyst/wax slurry and the various Polywax simulants used in the current study (Polywax 500, 655, 725, and 855, respectively) are displayed. For the FTS wax, hydrocarbons molecules range from carbon numbers 12 to +70. The majority of the hydrocarbons produced are straight-chain and paraffinic. The Polywax 500 is a commercial polyethylene polymer (9) with a narrow carbon number distribution with an nominal average molecular weight of 500 (note that in the previous DoE Technical Report (10), the Polywax 500 distribution was incorrectly displayed due to an analytical error). The subsequent Polywax product distributions are shifted to the left of the Polywax 500 and are substantially broader.

The test conditions for the “clean” wax tests were 4.2 m/s axial cross-flow velocity at 200 ^{o}C; the TMP was varied from 0.7 to 1.7 bar. The permeate flux of the Polywax 500 became stable after dropping from 0.9 to 0.65 lpm/m^2 after 5 days at 1.4 bar TMP. In Figure 7, the results of variable TMP study with the Polywax 500 are shown for 2-days and 6 days online. On average, the flux was consistently 0.25 lpm/m^2 lower after 6 days time-on-stream than that of the initial flux over the 0.7-1.7 bar TMP range tested.

Subsequent test results with the higher molecular weight waxes indicated shorter, if any induction periods. However, the filter element was not removed and regenerated after the initial Polywax 500 test. Once the Polywax 500 test was completed, the wax was drained from the system and a new batch the 655 was added and so on. In Figure 8, the permeate flux of the Polywax 725 is plotted over a 2-day period with a TMP range of 0.4 to 1.7 bar. The flux change over the one day period was less than 0.1 lpm/m^2 at 1.7 bar. For TMP lower than 1.4 bar, the change in flux is not detectable between the two data sets.

The effect of the wax molecular weight on the permeate flux (w/o catalyst) in shown in Figure 9. Power law functions were fitted for each data set at 0.7, 1.1 and 1.4 bar TMP. Overall the flux varied inversely with molecular weight according to the general formula:

$$Flux = k \cdot \frac{1}{MW^{\alpha}}$$

where power-law exponent, α , varied from 2.49 to 2.88;

and k = 3 x 10^7, 2 x 10^7, and 4 x 10^6 for 0.7, 1.1, and 1.4 bar TMPs, respectively.

The 1 µm cross-flow tube used for the clean wax test series (CF-12) was subjected to a static permeation test at 200 °C using the Durasyn 164, C_{30} oil before and after the filtration runs. The curve of the static membrane flux vs. TMP, as shown in Figure 10, can provide a snapshot of the tube's fouling condition. The filter media was fouled with polywax after the filtration tests without catalyst present. Previously, a simple bake out procedure at 500 °C was utilized to oxidize the Polywax remaining in the filter media pores. This had been an effective method to restore the filter media such that the static permeation rate was similar to that of a "new" tube. After the Polywax tests, it was decided to lower the bake out temperature to 450 °C in order to gauge the sensitivity of temperature on the effectiveness of the procedure. As shown in Figure 10, the 450 °C procedure restored about 50% of the media permeability. A subsequent bake out at 500°C increased the tube's permeability to approximately 60% of the "new" condition.

__Filtration Tests with Polywax 500/655 Activated Catalyst Slurry.__ The method used to determine slurry particle size distribution has been shown to have severe limitations. Slurry samples taken from the filtration unit had to extracted in o-xylene to remove the wax residue before being submitted for particle size analyses. Problems were encountered in recovering catalyst samples in the extraction thimbles (rated for 0.8 µm); Over 30-50% of the catalyst particles passed through the extraction thimble indicating substantial attrition of the particles. Also, we reported that qualitative particle settling tests indicated that catalyst attrition is changing the slurry properties over the time-scale of the filtration tests.

Accordingly, a test run using iron catalyst that had been activated in a CSTR system was initiated. Approximately 700 g of a iron was activated in two batches with a 1-liter CSTR. The activation conditions were maintained at 270 °C and 12 bar for 48 hours under a CO atmosphere. A wax mixture of the 81.3% Polywax 500 and 18.7wt% Polywax 655 was used as the slurry simulant in order to obtain a melting point to a typical FTS reactor wax (with melting point of approximately 95°C). The resulting activated slurry was added to a like Polywax mixture in the filtration unit such that a 9 wt% slurry was obtained. It was anticipated that the phase change to the carbide form during CO activation in addition to the increased physical attrition from the CSTR agitator would result in a dramatic decrease in catalyst particle size. In Figure 11, the permeate flux for the activated catalyst slurry is plotted versus time-on-stream. The flux stabilized to less than 0.2 lpm/m^2 over a 24 hour period as compared to 6 days with the unactivated catalyst. Previously, with the unactivated catalyst, the permeate quality was consistently less than 1 ppm as Fe; Consequently, the permeate had a bright white appearance. In contrast, the permeate obtained with the activated slurry was tinted brown, but considerable lighter than the catalyst slurry sample as shown in Figure 12. Thus, the iron content of the permeate was measured in the range of 18-30 ppm. TEM analysis of both the permeate and slurry samples are ongoing and should be available in the next quarterly technical report.

CONCLUSIONS

The initial membrane fouling experienced with the unactivated catalyst is likely due to changes in the particle size distribution over time. Although the high molecular weight waxes can apparently foul the filter media, the test results for waxes with molecular weight less than 855 g/mole have shown this effect to be minor compared to that of particle size changes.

The permeation flux with activated iron catalyst became stable after only 24-hours. However, the permeate quality suffered in terms of the iron content. Further control tests will be required to determine if the slurry particles were finer due to chemical or mechanical-based attrition.

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FIGURES for Task 1.1 & 1.2

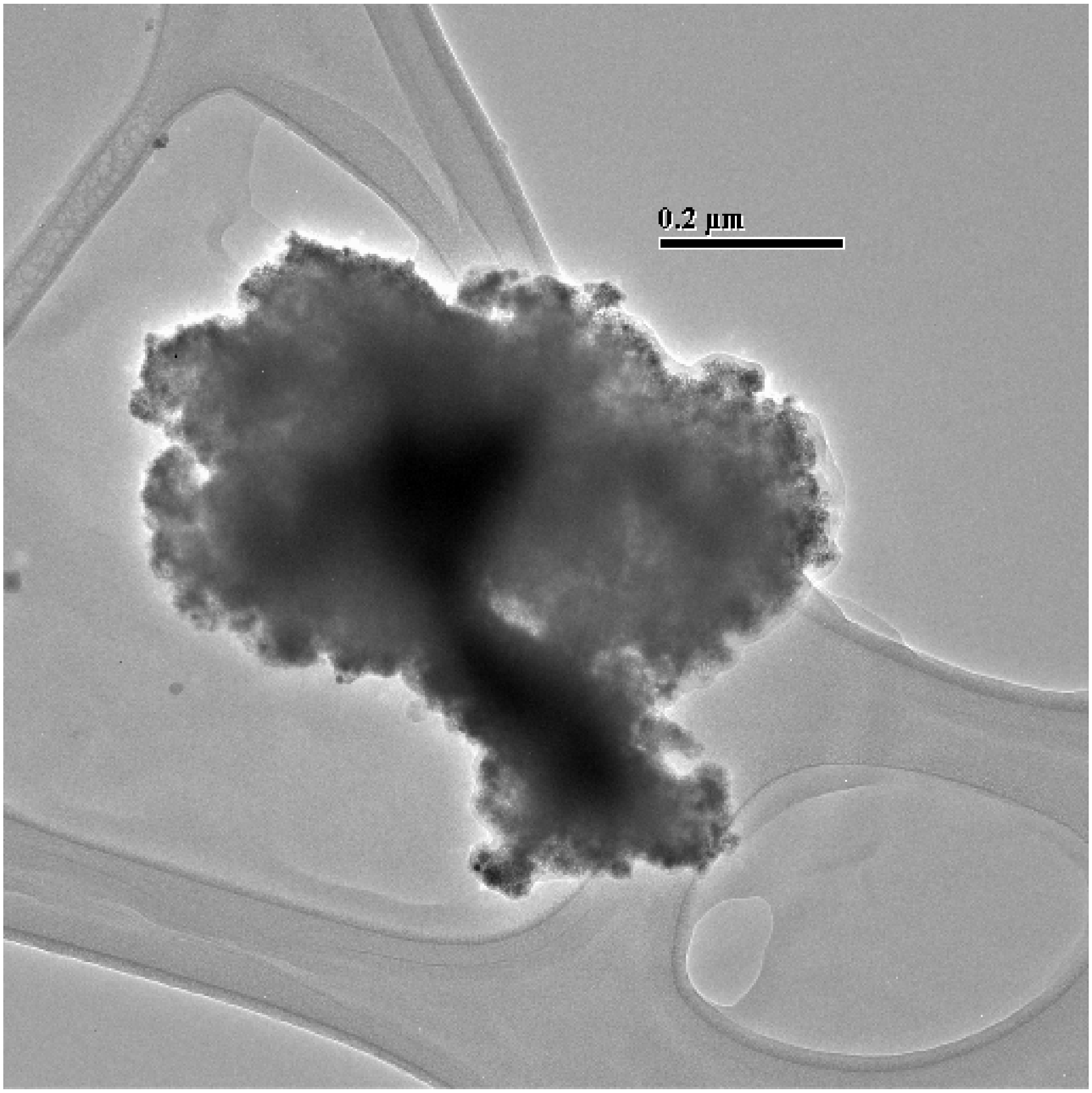

Figure 1. TEM Micrograph of an Iron Catalyst Particle in a Wax Slurry.

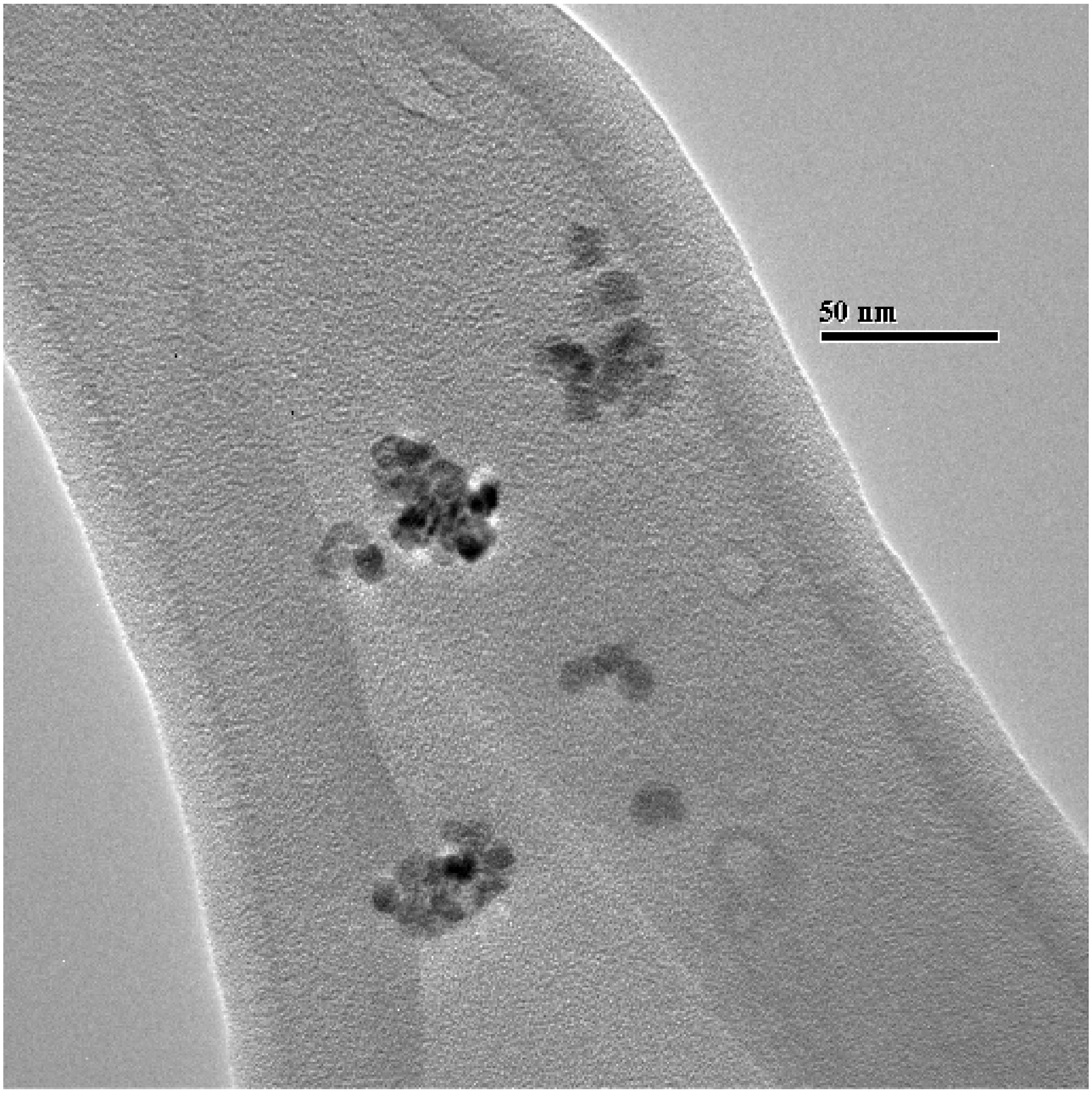

Figure 2. TEM Micrograph of Iron Catalyst Crystallites.

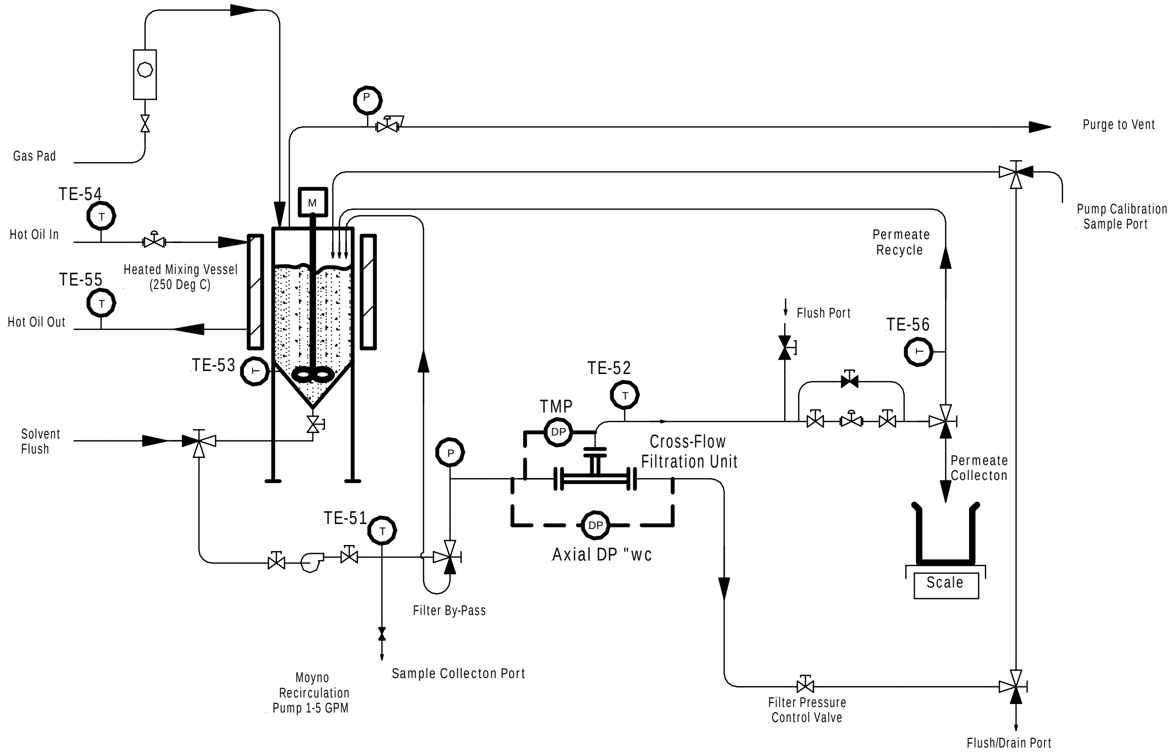

Figure 3. Schematic of the filtration test platform.

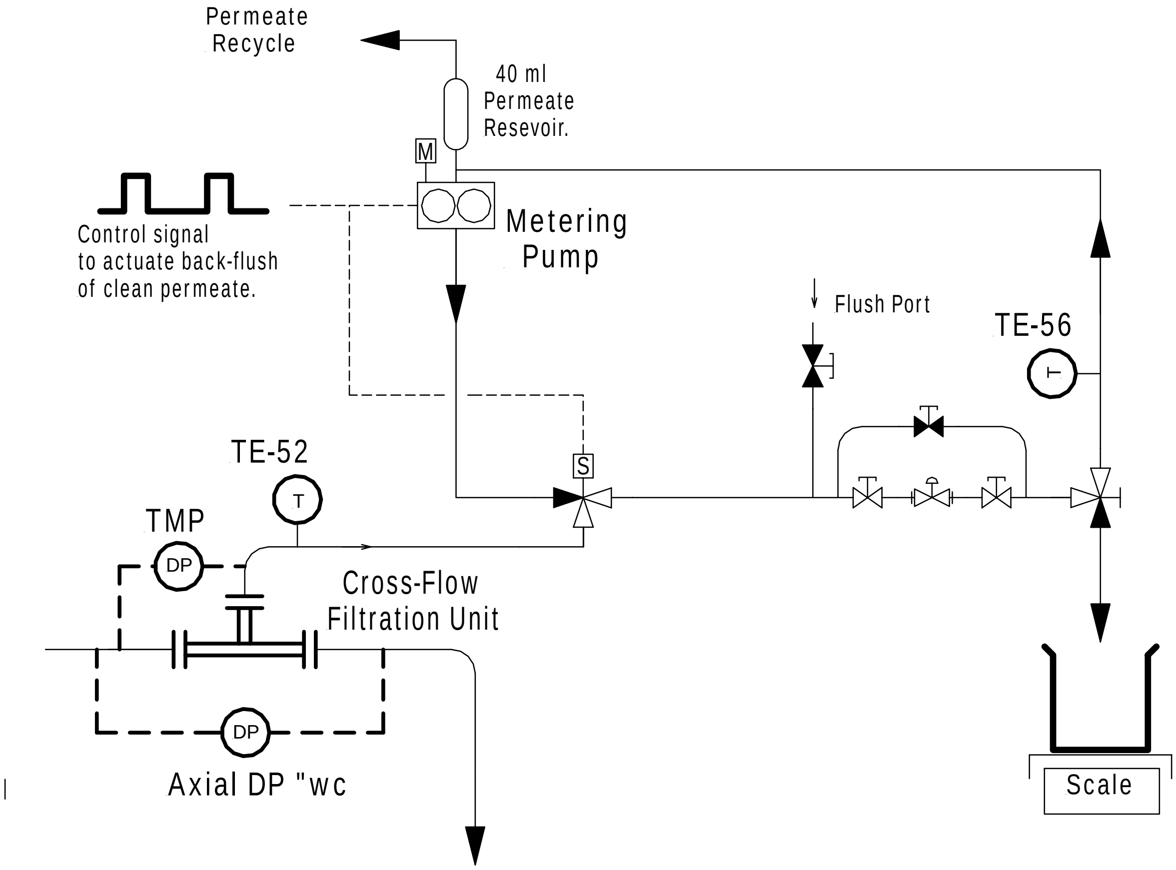

Figure 4. Schematic of the Permeate Back-Pulse System.

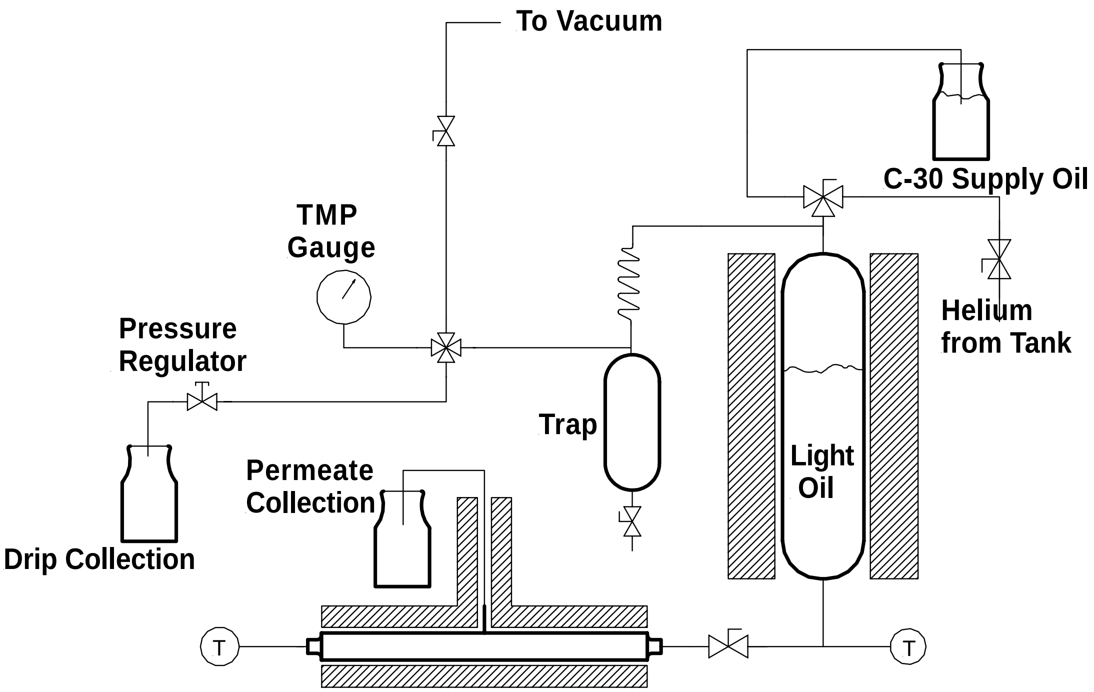

Figure 5. Schematic of the Static Permeation Test Apparatus.

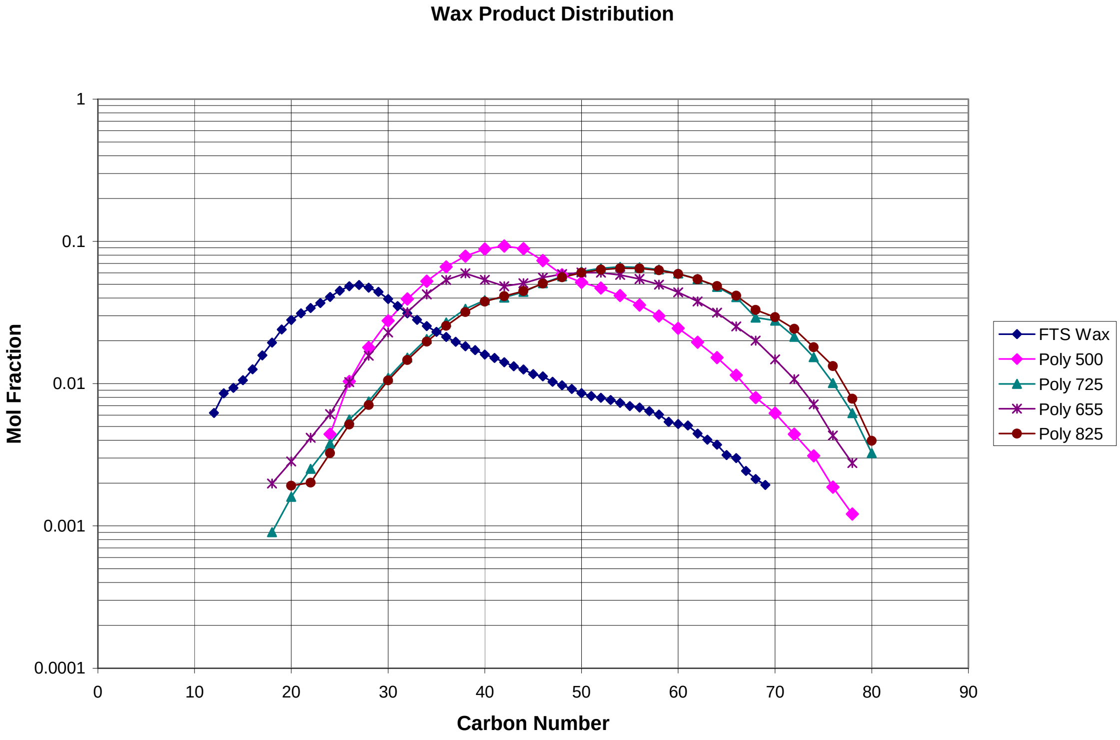

Figure 6. Comparison of Carbon Distribution Plots

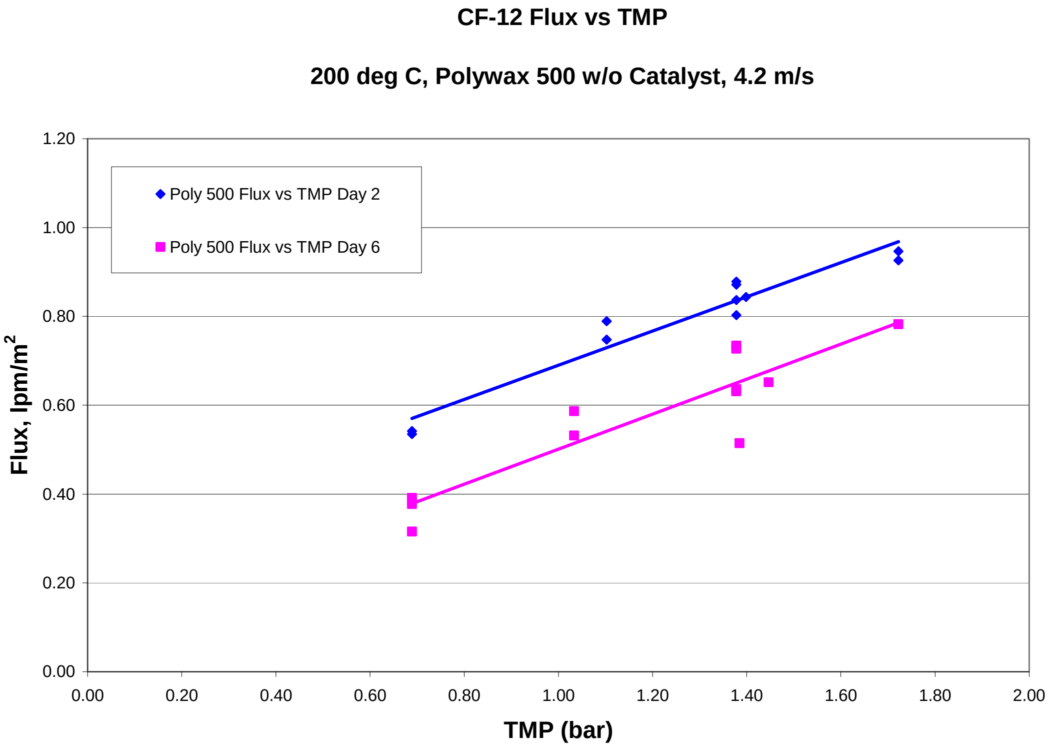

Figure 7. Polywax Flux vs. TMP w/o Catalyst

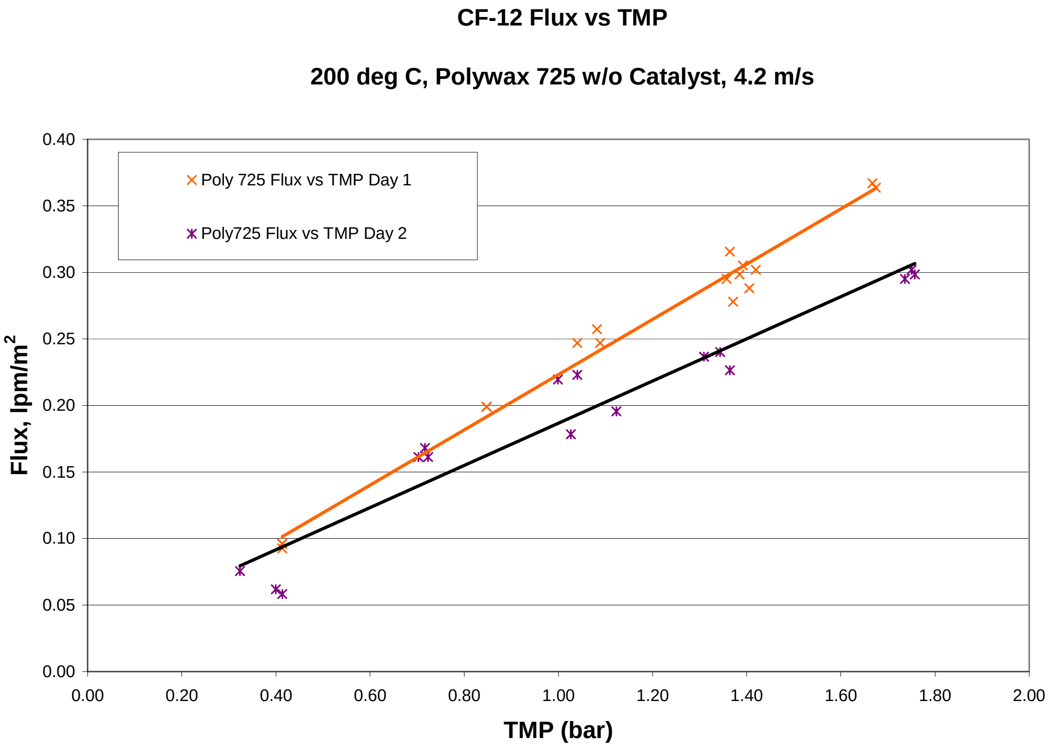

Figure 8. Polywax 725 Flux vs. TMP w/o Catalyst

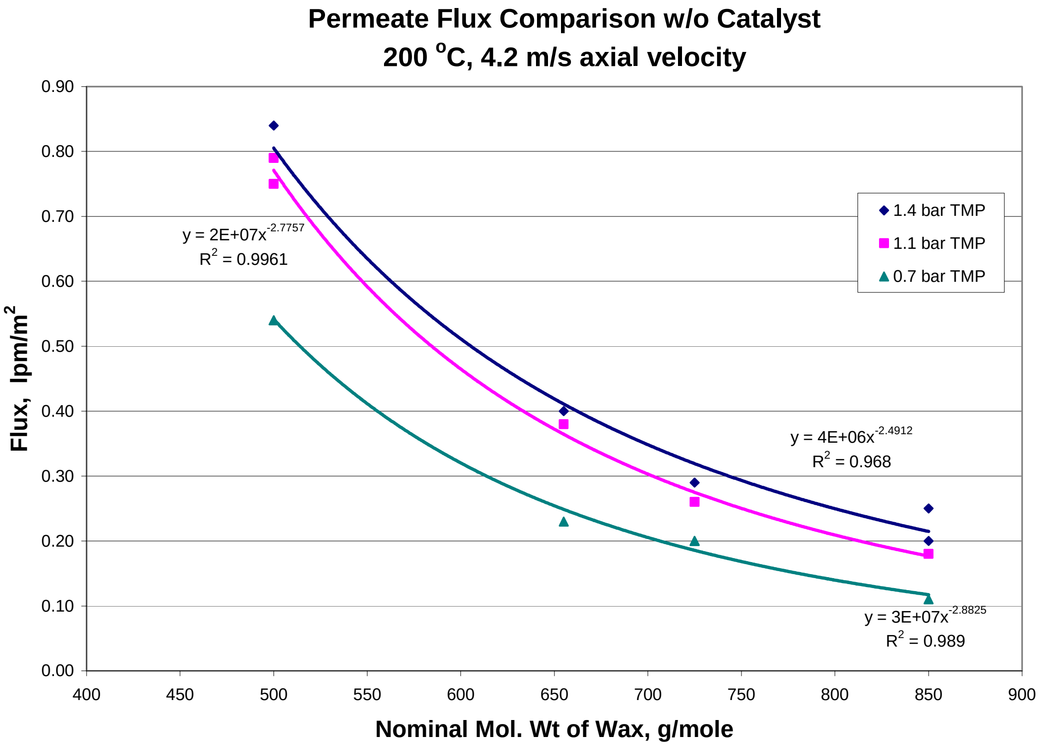

Figure 9. Effect of Molecular Weight on Permeation Flux

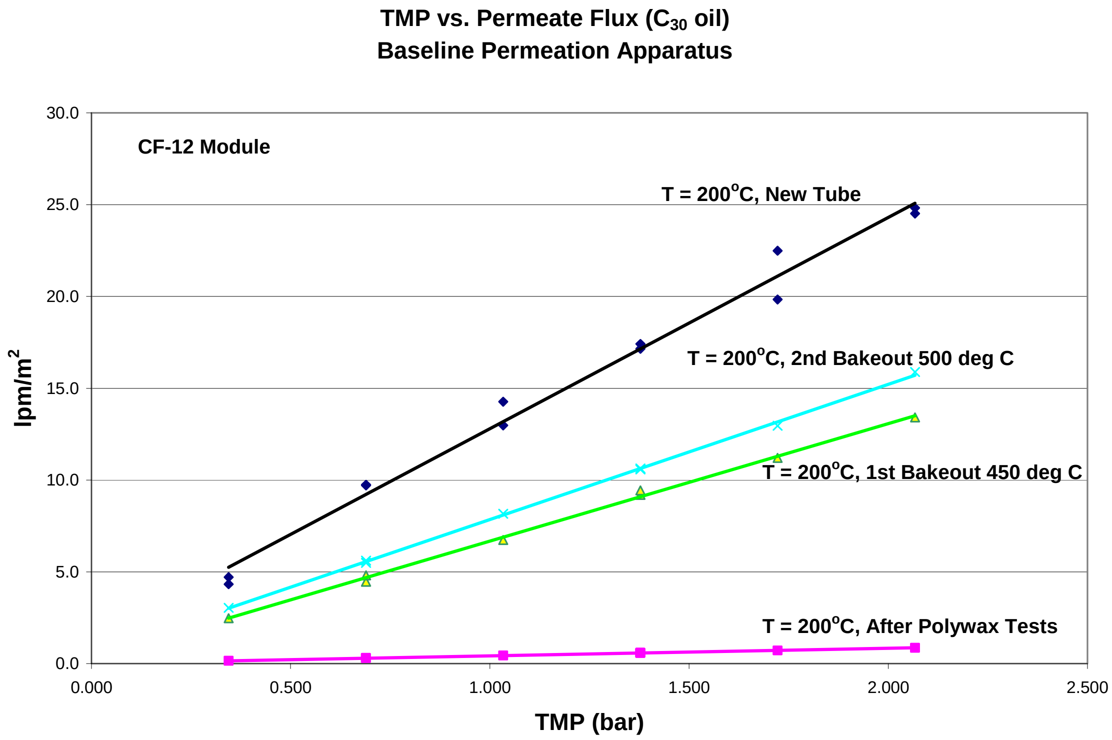

Figure 10 . Static Permeation Flux of 1.0 μm tube with Durasyn 164.

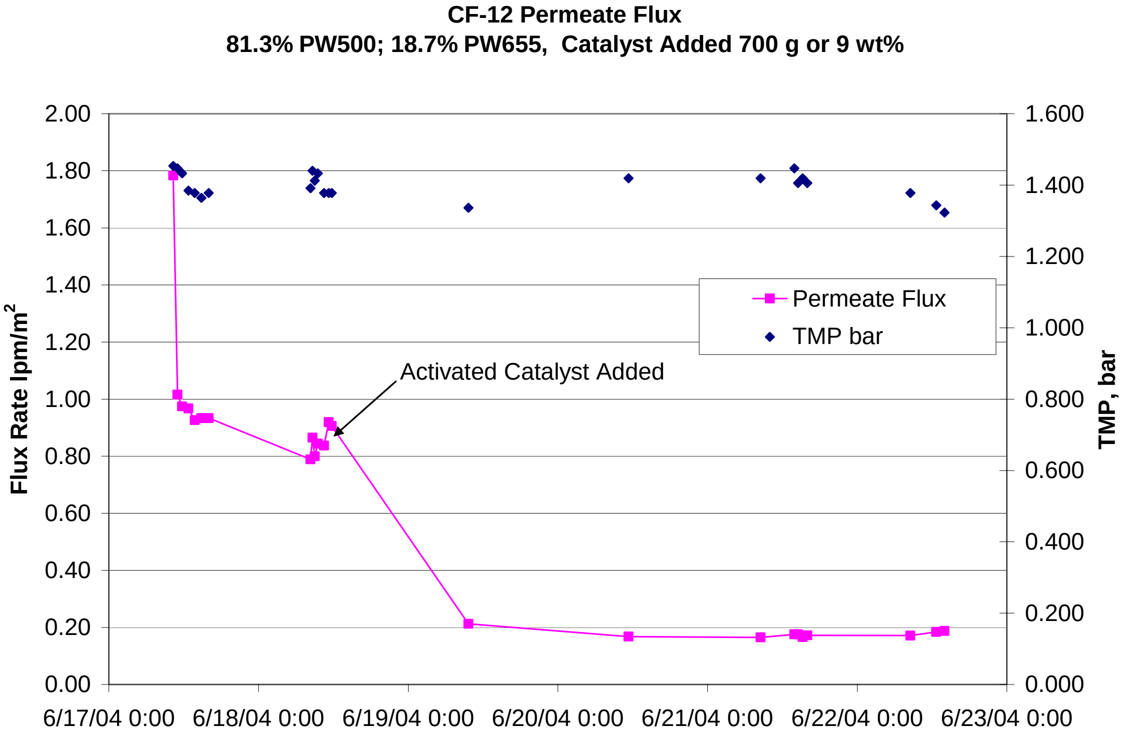

Figure 11. Permeation Flux vs. Time, Activated Catalyst

Figure 12. Activated Slurry (l) and Permeate (r) from Activated Catalyst Test.

Task 1.3. Filtration studies with doping of olefins and alcohols (CAER)

No work scheduled for this task during the current reporting period.

Task 1.4. Ultra-fine Iron Filtration (CAER)

No work scheduled for this task during the current reporting period.

Task 1.5. Development of Filter media cleaning procedure (CAER)

No work scheduled for this task during the current reporting period.

Task 1.6. Chemical and physical characterization of slurry and filtrate

INTRODUCTION

Insight into the chemical and physical changes of the catalyst associated with the attrition mechanism is being studied through the use of appropriate characterization techaniques. One proposed hypothesis that has received considerable attention is that Fe is lost from the surface of the catalyst as iron carbides (possibly the working active surface phase), which can block the filters, resulting in a deleterious rise in filter pressure drop, as well as decreased filtering capacity. This is typically referred to as "chemical attrition" (1,2). We have chosen rigorous characterization as a means to attempt a validation of this type of attrition process (3). In this quarter, EXAFS and XANES synchrotron methods were used to characterize the chemical state of the Fe species present in a working Rb-promoted Fe-based catalyst. In this quarterly report, results of EXAFS analysis are reported.

Furthermore, we continue to use indirect approaches to elucidate the active Fe surface phase. It is well established that Group I metals promote the Fischer-Tropsch reaction catalyst by iron (4). Rubidium is one particular Group I atom that can be studied at Brookhaven beamline X-18b by EXAFS. Therefore, we have attempted to further understand the active phase of Fe by examining the local structure surrounding Rb (3).

The work was conducted in part to refine our analytical methods which will be used in the near future to characterize used catalyst slurries. In March, 2004, CAER researchers visited the synchrotron at Brookhaven National Laboratory, Beamline X-18b, and carried out EXAFS/XANES studies at the K-edge of Fe on both Fe-based catalysts, as well as reference materials, including an Fe metallic foil, Fe_2O_3, Fe_3O_4, and the Fe-carbide reference. The two Rb promoted catalysts were also examined at the K-edge of Rb.

EXPERIMENTAL

EXAFS. EXAFS measurements on references and catalyst samples were conducted at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (BNL), using beamline X18b equipped with a Si(111) channel cut monochromator. A crystal detuning procedure was employed to prevent glitches arising from harmonics. The second crystal of the channel cut monochromates is weakly linked to the crystal and slightly spring loaded. The other side is a picomotor, a very fine high pitch screw that turns by piezo, which allows for slight detuning of the crystal. The X-ray ring at the NSLS has a flux of 1E10 photons per second at 100 mA and 2.5 GeV, and the energy range capability at X18b is 5.8-40 keV. The catalysts were previously run in the CSTR until steady state conversion was achieved. Catalyst was suspended in the waxy FT matrix for analysis. EXAFS data were recorded near the K-edge of iron and the K-edge of rubidium after cooling under helium flow to liquid nitrogen temperatures. All EXAFS spectra were recorded at close to the boiling temperature of nitrogen in a cell to minimize the contribution from the dynamic Debye-Waller factor.

Data reduction of the EXAFS spectra was carried out with WinXAS (5). Standard data reduction was carried out by pre-edge background removal and normalization by division of the height of the absorption edge. Chi-data were obtained by considering the single scattering region after the edge jump. Appropriate splines based on the Nyquist criteria (6) were utilized to avoid the inclusion of excessive nodes that could destroy the data. After conversion to k-space, the Fourier transform was conducted to obtain the uncorrected radial distribution function.

RESULTS AND DISCUSSION

The catalyst studied in this reporting period was removed from a CSTR reactor under inert gas conditions and solidified in the FT wax matrix to preserve it for study by EXAFS and XANES. In this quarterly report, the EXAFS results are provided. Fourier transform magnitudes for the iron K-edge data are reported in Figure 1 and confirm the results of Mossbauer spectroscopy reported in the first quarterly report of 2004. The Fe-Fe coordination peaks match closely those of our iron carbide reference sample. This is true not only with regard to the first coordination shells (2.2 and 2.5 angstroms), but to those of higher shells (2.9 and 3.4 angstroms) as well. In addition, it is clear that the peaks in the Fourier transform do not coincide with any of the oxidized Fe phases (e.g., Fe_2O_3 and Fe_3O_4). Our EXAFS results are consistent with a similar phase evolution to iron carbide that was reported for a potassium-promoted Fe_2O_3 sample utilizing in-situ XANES (7).

The approach of R.J. Davis et al. (8) was utilized to analyze the Rb K-edge data. The rubidium oxide reference was prepared by decomposing RbOH in UHP helium in-situ and at 500^{o}C. As noted by Davis et al. (8), a peak in the Fourier transform magnitude spectra for the Rb-O interaction is readily observed if the Chi(K) data is truncated between 1.8 and 6.0 A^{-1}. The results obtained in Figure 2 were almost identical to the results of Davis et al. Likewise, the Rb-O interaction was also observed for the

5%Rb catalyst, and the result coincided with the rubidium oxide reference precisely, as shown in Figure 2.

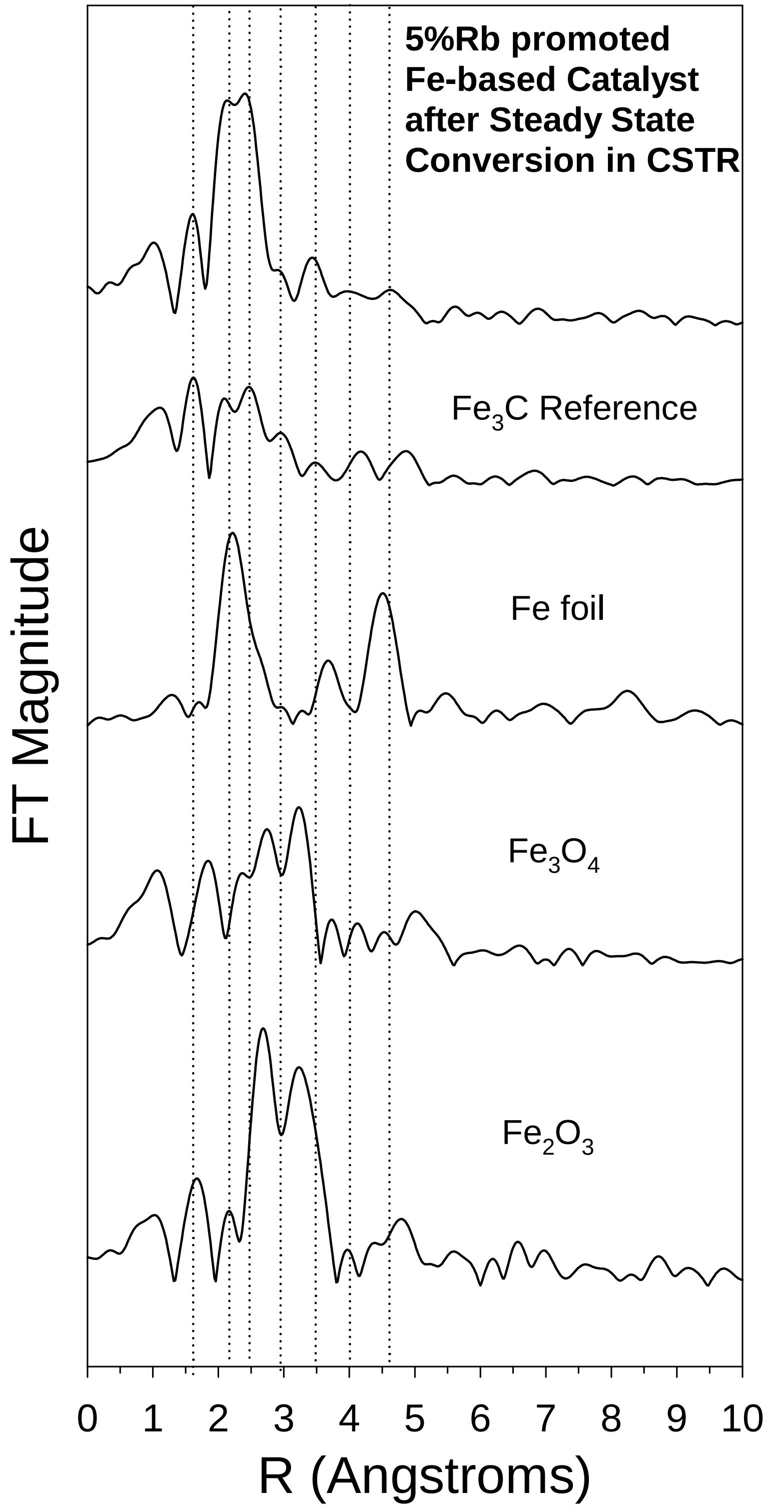

Figure 1: Fe K-edge results. Fourier transform magnitudes of references and the 5% Rb promoted catalyst.

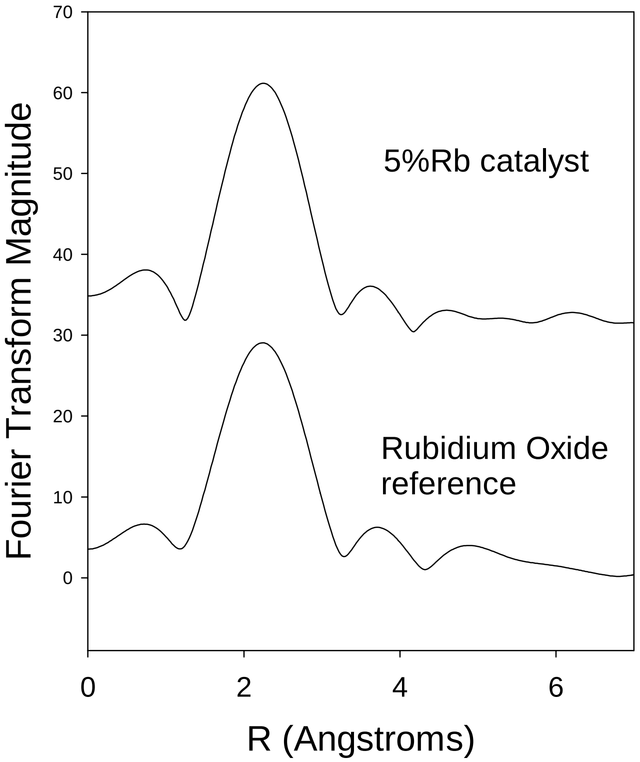

Figure 2: Rb K-edge results. Fourier transform magnitudes of rubidium oxide references and the 5% Rb promoted catalyst. One broad peak associated with the Rb-O interaction in the first shell is observed for both samples. A short k-range between 2.0 and 6.0 Angstroms was utilized in this preliminary study.

CONCLUSIONS

Preliminary characterization by EXAFS confirmed our previous results of Mossbauer spectroscopy that a major component of the reduced, activated catalyst is Fe carbide. An attempt was made to elucidate the Fe active phase by examining the local structure surrounding the Rb promoter by EXAFS. However, only a Rb-O interaction was found, suggesting that on average, the Rb clusters are too large to obtain information on a rubidium-iron carbide interaction. The results confirm EXAFS as an appropriate technique for determining chemical information on the Fe phases present in the working catalyst.

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Task 2. Phase II Bubble Column Pilot Plant Studies

No work scheduled for this task during the current reporting period.

PATENTS, PRESENTATIONS AND PUBLICATIONS

Patents Issued 2004

James K. Neathery and Burtron H. Davis (2004), “Bubble Column Apparatus for Separating Wax from Catalyst Slurry.” U.S. Patent 6,762,209.

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Jacobs, G.; Chenu, E.; Patterson, P.M.; Williams, L.; Sparks, D.E.; Thomas, G.; and Davis, B.H. “Water-gas Shift: Comparative Screening of Metal Promoters for Metal-ceria Systems and Role of the Metal,” Applied Catalysis A: General 258 (2004) 203.

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Presentations and Symposia 2004

Jacobs, G; Patterson, P.M.; Chaney, J.A.; Conner, W.; Das, T.K.; Luo, M.; and Davis, B.H., "Fischer-Tropsch synthesis: Influence of Reduction Promoters on Cluster Size and Stability of Co/Al2O3 Catalysts for GTL,"Anaheim, CA, Am. Chem. Soc., Div. Petr. Chem. 49 (2004) 186.

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Jacobs, G., Patterson, P.M., Chaney, J.A., Conner, W.A., Das, T.K., and Davis, B.H., "Fischer-Tropsch Synthesis: Influence of Cluster Size and Promoters on Reoxidation Phenomena Associated with Co/Al_2O_3 Catalysts for GTL," 13th International Congress on Catalysis, July 11-15, 2004, Paris, France.

TRAVEL

Gary Jacobs and Burtron H. Davis attended and presented at the ACS spring national meeting in Anaheim, California in March of 2004, the AICHE spring national meeting in

New Orleans, LA in April of 2004, and the 13th International Congress on Catalysis in Paris, France in July of 2004. Burtron H. Davis also attended the Isotope Meeting in Poitiers, France prior to the ICC meeting.